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THE OXIDATION, DECOMPOSITION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

XXIV. THE ADVERSE EFFECT ON THERMAL EFFICIENCY OF THE ENDOTHERMIC CRACKING REACTION REQUIRED FOR THE COMPRESSION IGNITION OF PARAFFIN HYDROCARBONS

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XXIV. THE ADVERSE EFFECT ON THERMAL EFFICIENCY OF THE ENDOTHERMIC CRACKING REACTION REQUIRED FOR THE COMPRESSION IGNITION OF PARAFFIN HYDROCARBONS[1]

By R. O. King[2] and A. B. Allan[3]

ABSTRACT

The adverse effect on thermal efficiency of the decomposition (cracking) reaction required to produce the nuclei which enable a carburetor engine to run with ignition by compression is demonstrated by the experiments described in the text. For this purpose, values of indicated thermal efficiency determined when using normal varieties of pentane, hexane, and heptane with ignition by compression are compared with those determined when using benzene in comparable conditions of mixture strength and compression ratio. In these conditions benzene does not decompose during compression to the extent required to produce nuclei of ignition and mixtures with air require a spark for ignition, unless in contact with a surface at an igniting temperature. Values of indicated thermal efficiency determined when using the paraffins were from 7 to 8% lower than those obtained when using the benzene, mixture strength being 20% weak in both cases. The adverse effect increased with increase of mixture strength. It was approximately 10% for correct mixtures. Furthermore with nuclear ignition the paraffins could be used at weaker mixtures than was possible for benzene with spark ignition. The experiments indicate that the nuclear ignition of paraffin–air mixtures richer than 20% weak is a single stage effect due to carbon derived from cracking of the paraffin. The ignition of leaner mixtures occurs in two stages, the first being initiated by nuclei of a resinous nature. Residues of these nuclei mixed with carbon formed an adherent coating on surfaces not exposed directly to flame such as the lands between piston rings. The rings became firmly stuck in their grooves which had become filled with the residues. The experiments were carried out at diesel engine compression ratios and the results are believed to be of interest in respect of the fundamentals of combustion in that type of engine.

INTRODUCTION

The operation of a C.F.R.-F2 carburetor engine with ignition by compression when normal varieties of heptane, hexane, and pentane were used as fuels was described in Part XXI (4). The compression ratios required for ignition were comparable with those of diesel engines, as would be expected. They varied with mixture strength and the length of the carbon chain of the paraffin molecule. It was always possible to adjust compression ratio for a maximum power output at any particular mixture strength. The experimental results were consistent with the nuclear theory of ignition, as stated in Part IV (3), namely that the finely divided carbon required for the nuclear ignition of the end gas in a spark ignition carburetor engine is provided by the decomposition (cracking) of paraffinic fuel at the high temperatures and pressures attained.

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On the other hand, it was shown by experiments described in Part XXII (5) that a hydrocarbon fuel such as benzene does not decompose at diesel engine compression ratios in a manner to provide nuclei of ignition. Decomposition if it occurred would, in the first stage, yield hydrogen and diphenyl which is a gas at the required temperatures. Thus in the experiments mentioned, a spark was always necessary for controllable ignition, and uncontrolled ignition tending to develop into preignition occurred when a spark plug core attained the requisite high temperature.

The experimental results of Parts XXI and XXII were in accordance with the well-known tendency of normal paraffins to decompose more readily to carbon and other final products than members of the aromatic series, in similar conditions of temperature and pressure. The decomposition reaction is endothermic and if it occurs during compression in an engine, thermal efficiency would be affected adversely by the heat absorbed. Thus it will be shown by the comparison made in this Part that (1) the thermal efficiencies obtained for the paraffins with compression ignition are lower than those obtained for benzene with spark ignition and (2) the paraffins with compression ignition can be used at mixtures leaner than those at which benzene can be ignited by spark ignition and that in these leaner mixtures nuclear ignition occurs in two stages, the first stage appearing to be due to nuclei containing resinous substances.

Arrangement of Text

Subsequent text is in numbered sections for convenience of reference. The normal paraffins are, when convenient, described as detonating fuels. The terms compression ratio, optimum compression ratio, mixture strength, indicated thermal efficiency, and indicated mean effective pressure are, when convenient, abbreviated to C.R., Opt.C.R., M.S., I.T.E., and I.M.E.P. respectively. Chemically correct mixtures of fuel and air are described as "correct" in the text but the abbreviation "C.C.M." is used on graphs. Values of compression ratio are abbreviated to a single number. Opt. C.R. is the value at which power output is a maximum at a particular mixture strength. Compression ignition is, when the context is fitting, described as nuclear ignition. It is to be understood that values for I.M.E.P. given in the text or on graphs are in pounds per square inch and that values given for engine speeds are revolutions per minute.

Heat Load

This term, although not commonly used, has been adopted as a convenient expression for the factors which determine the mean temperatures attained by surfaces in the combustion chamber, see discussion Part XXII (5, pp. 45–48). Primary factors are: the heat arising from compression of the fuel–air mixture and residual gases and the heat content of the entering mixture; plus the heat liberated by combustion of the fuel; minus the proportion converted into work, that absorbed by vaporization of fuel after admission, and that rejected to the exhaust. The heat load, expressed in B.t.u. per min. at parti-

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cular values of C.R. and M.S., is then directly proportional to engine speed at constant volumetric efficiency. It will then be equal to the rate of heat conduction through the materials of the combustion chamber when engine temperatures have reached a steady state. The surface temperatures attained by materials in the combustion chamber will then depend on the temperature gradients in them. These in turn will depend on their thermal conductivities, the length and the nature of the heat path to the cooling medium, and its temperature. The surfaces of indirectly cooled parts of the combustion chamber are most liable to attain temperatures that will affect the combustion of the fuel. These are: the valves, the center of the piston crown, the ceramic core of the spark plug, and its electrodes. Any one of these, with an extremely heavy heat load, may attain the temperature required for some degree of flameless combustion of the fuel, but in normally aspirated water cooled engines, the surfaces liable to attain an igniting temperature in respect of the fuel–air charge are those of the exhaust valve, the ceramic core of the spark plug, and in some cases those of its electrodes—the exhaust valve because it is off its cooling seat during the exhaust stroke, the head and the lower part of its stem being then in the path of the exhaust gases, and the ceramic core of the spark plug because of its low thermal conductivity.

1. RATES OF BURNING OF PARAFFIN–AIR MIXTURES WITH NUCLEAR IGNITION AND OF BENZENE–AIR MIXTURES WITH SPARK IGNITION

Paraffin–Air Mixtures

Experiments with the paraffins, described in Part XXI (6), were carried out in engine conditions of a subnormal charge density, an air supply temperature of 50° F., a jacket coolant temperature of 100° F., and an engine speed of 400. That is, the heat load on the engine was relatively low and the corresponding low cycle temperature would be expected to be of favorable effect on indicated thermal efficiency. Ignition was by compression and maximum power output was obtained for values of the C.R. of 8.5, 9.6, and 10.0 for correct mixtures with air of heptane, hexane, and pentane, respectively. The characteristics of combustion are illustrated by the typical pressure–time diagrams of Fig. 1, taken when using heptane as the fuel. Short vertical lines have been added to the diagrams to mark the "blips" fed into the electronic circuit at 10° intervals of crank revolution by a notched timing wheel. The line at top dead center is marked t.d.c. The irregularity of spacing is due mainly to the inertia of rotating parts, including the armature of the direct connected generator, which was such that the speed of rotation of the blip timing wheel attached to the outboard end of the armature shaft was affected by cyclic changes of pressure on the piston. A relatively thick indicator diaphragm was used when taking diagram A, because of the high pressure developed. Therefore the pressure scale differs from that of diagram B. Both diagrams were taken with a "Sunbury" indicator and consequently the pressure scales are non-linear.

It will be seen by reference to the diagrams that nuclear ignition occurred in a single stage for mixtures correct and 20% weak. It occurred in two stages

for mixtures weaker than can be used for benzene with spark ignition. The characteristics of the two-stage effect will not be discussed at present. Diagram A, for a correct heptane–air mixture, shows that compression pressure ceased to rise appreciably at approximately 12° before t.d.c. and remained substan-

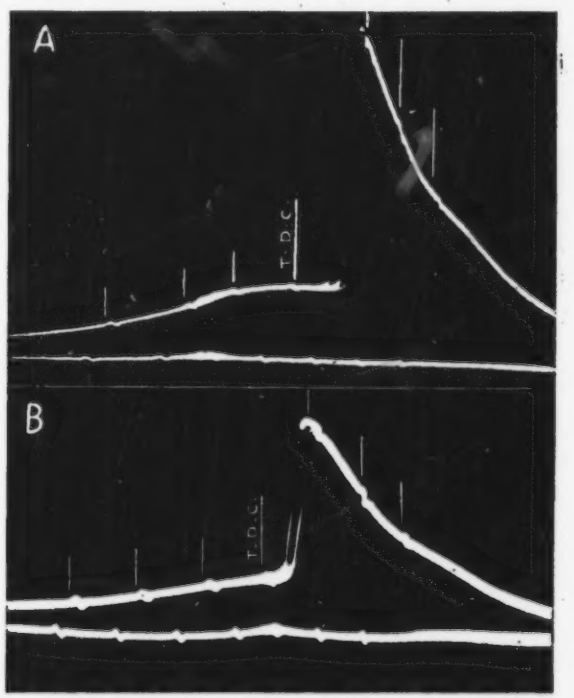

FIG. 1. Typical diagrams for the combustion of paraffins with nuclear ignition.
A. Correct mixture, C.R. 8.5.
B. 20% weak mixture, C.R. 9.1.
Heptane.

tially constant until 7° after. The failure of pressure to rise during 19° of crank revolution is attributed to the absorption of heat by the decomposition reaction required to produce nuclei of ignition. It is the familiar "delay angle" which is a characteristic of the combustion of paraffinic fuels in diesel engines.

The combustion characteristics of the nuclear ignition of the 20% weak heptane–air mixture are shown by diagram B. This diagram, like diagram A, was taken when C.R. was adjusted for maximum power output and it will be

noted that, as for diagram A, this was obtained when combustion pressure attained a maximum value at approximately 10° after t.d.c. The Opt. C.R. was 9.1 and it appears from the compression line of the diagram that decomposition of the heptane at the gas temperatures and pressures attained accordingly began earlier than when the C.R. was lower, at the value of 8.5, as required to obtain maximum power output for a correct mixture, diagram A. A definite value cannot be assigned to the delay angle for the weaker mixture in the absence of a diagram for compression of air only. Both diagrams show that the pressure rise due to combustion started sharply at the end of the delay period, presumably on the attainment of the requisite concentration of nuclei in the part of the combustible mixture at maximum temperature. That would be the part adjacent to the exhaust valve, the spark plug having been replaced by a mild steel blank. The time interval between nuclear ignition and the attainment of maximum combustion pressure was 3° of crank revolution or 0.00125 sec. If the distance of flame travel is taken from the center of the exhaust valve to the farthest point on the combustion chamber wall, the velocity would be 150 ft./sec. In the circumstances and in the cool running conditions, the engine ran on a nearly exact constant volume cycle of relatively low temperature with maximum combustion pressure occurring at the piston position for maximum power output. Indicated thermal efficiency should therefore have approached the ideal value as nearly as possible in practice, *but for the loss during compression and prior to ignition of the heat absorbed by the decomposition reaction required to produce an igniting concentration of nuclei.* This loss would affect compression pressure adversely with the result that the engine would be running on a compression ratio lower than the measured value which is used when calculating thermal efficiency.

Benzene–Air Mixtures

The slow burning characteristic of benzene and its failure to decompose in the end gas of a spark ignition engine to provide the nuclei of ignition required for "detonation" are attributed to the stability of its molecule. A further consequence of slow burning is that in the experiments described in Part XXII (5), benzene was not a good fuel for the C.F.R. engine when operated in conditions of low heat load, in that when an attempt was made, by raising the compression ratio, to obtain maximum thermal efficiency for weak mixtures, the engine tended to run on a constant pressure instead of a constant volume cycle (5, pp. 27–28). An approach to a constant volume cycle was obtained for mixtures in the neighborhood of correct on increasing the heat load by raising the air supply from 50 to 140° F., the jacket coolant from 100 to 140° F., the speed from 400 to 900 r.p.m., and the charge density from 64% of normal to normal. It was estimated that these increases had resulted in raising the initial temperature of compression from 100 to 200° F. and the final temperature from 740 to 930° F. when the C.R. was 8.0 (5, p. 43). The characteristics of combustion obtained accordingly at the C.R. of 8.0 are illustrated by the typical indicator diagrams of Fig. 2. The time of passage of the spark is shown on the diagrams by the small downward blip fed into the electronic circuit. Optimum

spark timing was always used and it will be seen by reference to diagram A, that the spark occurred at 11° before t.d.c. and maximum pressure at 13° after. When a 26% weak mixture was used, diagram B, optimum spark timing was 21° in advance of t.d.c. and maximum combustion pressure occurred at 15° after.

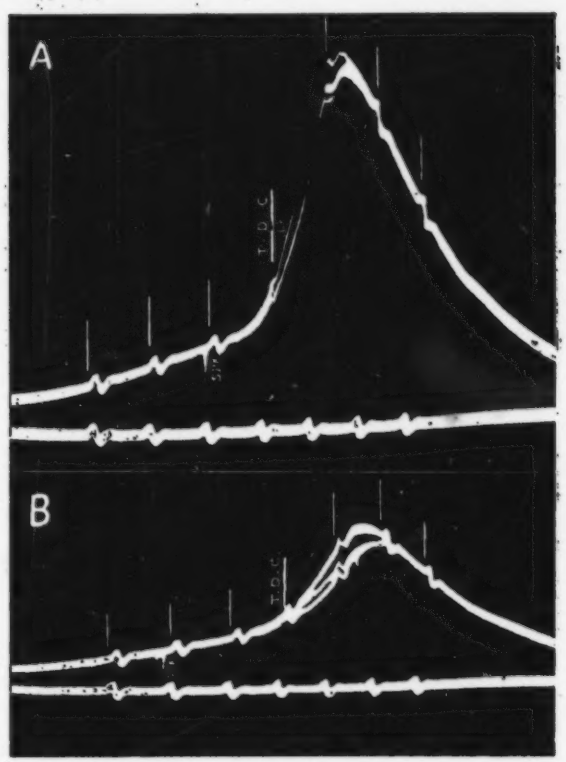

FIG. 2. Typical diagrams for the combustion of benzene with spark ignition.
A. Correct mixture, C.R. 10.
B. 26% weak mixture, C.R. 8.

The long burning time required for the combustion of the benzene–air mixture even after increasing inflammability by raising the temperature of the charge at the time of spark ignition is in sharp contrast with the 3° of crank revolution required for combustion when nuclei of ignition had been provided by the preflame decomposition of a normal paraffin.

II. NUCLEAR IGNITION AND THE RELATION BETWEEN INDICATED THERMAL EFFICIENCY AND COMPRESSION RATIO; PENTANE, HEXANE, AND HEPTANE

It was shown by experiments with the normal paraffins used in engine running conditions in which nuclear replaced spark ignition that the relation between Opt. C.R. and M.S. is represented by a W form of graph instead of the U form obtained when ignition is by spark at relatively low values of C.R., Part XXI (6). The W form of graph shown at A, Fig. 8, is for pentane–air mixtures and is similar in form to those obtained when using hexane and heptane. These will be given later as required. The corresponding relation between I.T.E. and

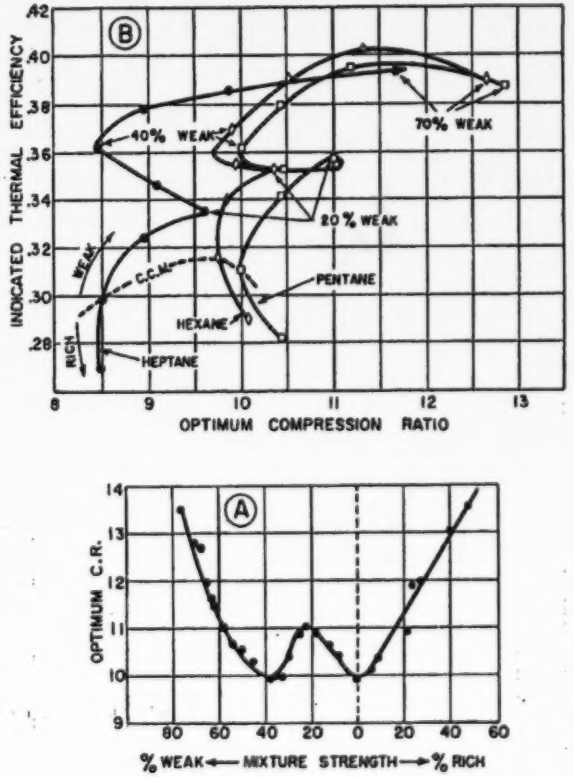

FIG. 3. A. Typical relation between Opt. C.R. and M.S. shown by experiments with pentane. B. Relation between I.T.E. and C.R. with diminishing M.S.; heptane, hexane, and pentane.

C.R. for mixtures with air of pentane, hexane, and heptane ranging from 10% rich to 70% weak, as determined by experiments described in Part XXI, are exhibited by the corresponding graphs, B, Fig. 3. They were not given earlier because comparable results for a non-detonating hydrocarbon with spark ignition were not then available. Experimental points are not shown on the graphs. They have been replaced by points indicating 10% changes of mixture strength. Correct mixtures are indicated by the broken line crossing the graphs.

Indicated thermal efficiency is shown by the graphs to have increased, as would be expected as Opt. C.R. was increased and mixture strength decreased from correct until it became 20% weak. An abrupt reversal of direction of the graphs then occurred and I.T.E. remained nearly constant over the mixture range 20 to 40% weak for both pentane and hexane. It will be noted however by reference to the A graph, that Opt. C.R. ratio diminished over this range of M.S. It appears therefore that the increase in I.T.E. normally due to a decrease of M.S. was just offset by the decrease in I.T.E. due to decrease of Opt. C.R. Nuclear ignition of heptane–air mixtures occurred at considerably lower compression ratios than were required for mixtures with air of pentane or hexane. The adverse effect on I.T.E. of decreasing Opt. C.R. over the mixture range 20 to 40% weak was, as shown by the graph, more than offset by the beneficial effect obtained on decreasing the M.S.

The graphs for I.T.E. show that another abrupt reversal of direction occurred for all three fuels when the mixtures became 40% weak. Then as mixture strength was further decreased and Opt. C.R. increased, I.T.E. increased slowly to a maximum value and then diminished. This characteristic is related to the occurrence of ignition and combustion in two stages, with the first beginning before t.d.c., Part XXI (6, Figs. 3 and 4).

The decomposition of heptane in correct mixtures with air, to provide nuclei of ignition at a C.R. of 8.5 whereas values of C.R. of 9.6 and 10 were required to obtain a similar effect in respect of hexane and pentane respectively affords a rational explanation for the use of heptane to represent zero on the C.F.R.–A.S.T.M. knock rating scale.

III. THERMAL EFFICIENCIES: BENZENE

Indicated Thermal Efficiencies at Values of C.R. from 4 to 13

The values of I.T.E. for benzene–air mixtures varying from 20% rich to the weakest on which the engine would run, and at values of C.R. increasing from 4 to 13, as determined by experiments described in Part XXII (5), are given by the graphs of Fig. 4. The operating conditions were those of the "higher" heat load. There are three features of the experimental results of especial present interest:

(1) The I.T.E. at any particular C.R. increased continuously, although at a decreasing rate as M.S. was reduced, as would be expected, until it had attained a maximum value when it diminished rapidly as misfiring began.

(2) The M.S. for which a maximum value of I.T.E. was obtained diminished with increase of C.R., as shown by the inclined broken line crossing the graphs of the figure. That is, misfiring occurred with progressively weaker mixtures as compression ratio was raised. Thus at a C.R. of 13, smooth running without misfiring continued until the mixture became 35% weak, but at a C.R. of 4, misfiring began with mixtures leaner than 25% weak.

The I.T.E. obtained for a mixture weaker than that required for maximum thermal efficiency is therefore not regarded as a true value.

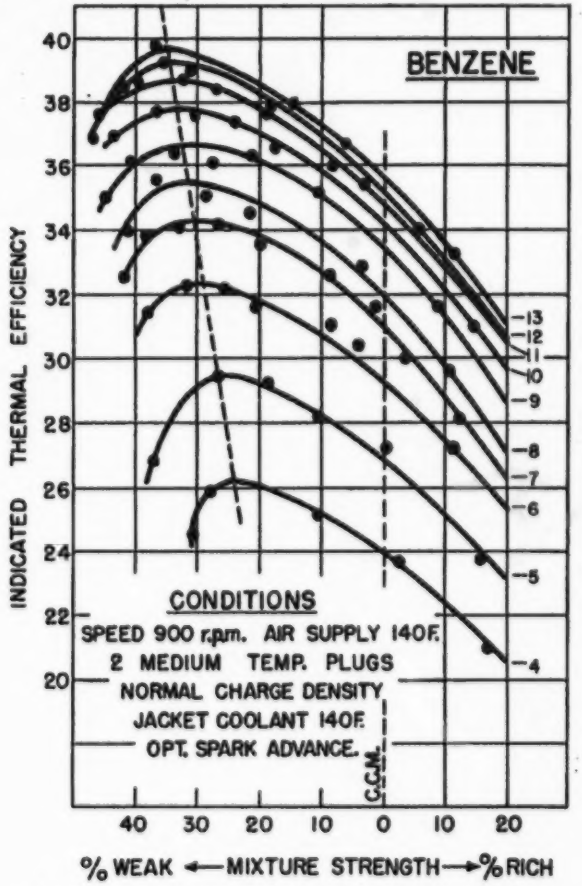

FIG. 4. Relation between I.T.E. and M.S. at values of C.R. of 4 to 13.

Indicated Thermal Efficiency as Affected by Heat Load

It was found as a result of an extensive series of experiments with benzene–air mixtures (5) in the low heat load conditions, that optimum values for I.T.E. over a wide range of M.S. were obtained when spark timing was fixed at 20° in advance of t.d.c. and C.R. always adjusted for maximum power output as M.S. was varied. The relation between Opt. C.R. and M.S. thus obtained is given by graph A of Fig. 5, and the corresponding values of I.T.E. by graph B.

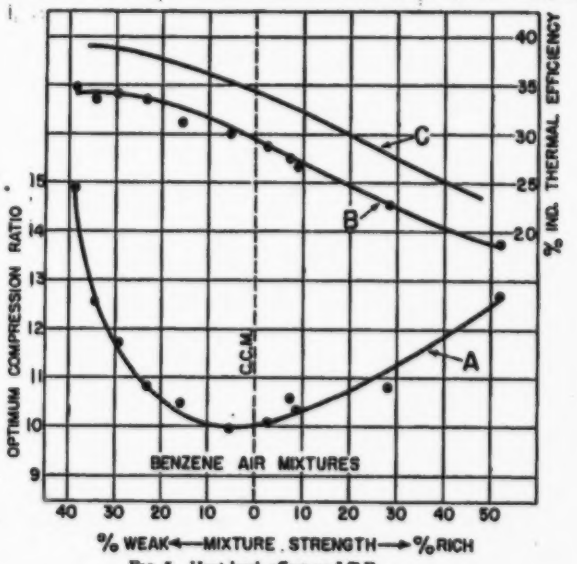

FIG. 5. Heat load, effect on I.T.E.
C. I.T.E. with high heat load.
B. I.T.E. with low heat load.
A. Common base of optimum C.R.

Now by making use of the data given by the graphs of Fig. 4, the I.T.E. values for similar values of M.S. and C.R. as determined in the running conditions of the higher heat load can be obtained. These are given by graph C of the figure and it will be understood that the values of I.T.E. shown by graphs B and C are derived from the common basis of Opt. C.R. and M.S. as represented by graph A. The noteworthy feature of the experimental results is that thermal efficiency increased on increasing the temperature of the cycle. This anomalous result is attributed to the increase in inflammability of the benzene–air mixture due to the increase of heat load and the consequent addition of the heat of combustion of the benzene to the working fluid at more nearly constant volume, this effect being great enough to more than offset the adverse effect of increasing the temperature of the cycle.

Indicated Thermal Efficiencies Compared with Ideal Values

The relation between I.T.E. and C.R. is given by graph A of Fig. 6, for benzene–air mixtures used in conditions of the low heat load and with ignition timing fixed at 20° in advance of t.d.c. A single hot spark plug, C.F.R.-8, was used. There is shown a just measurable increase in I.T.E. for an increase of

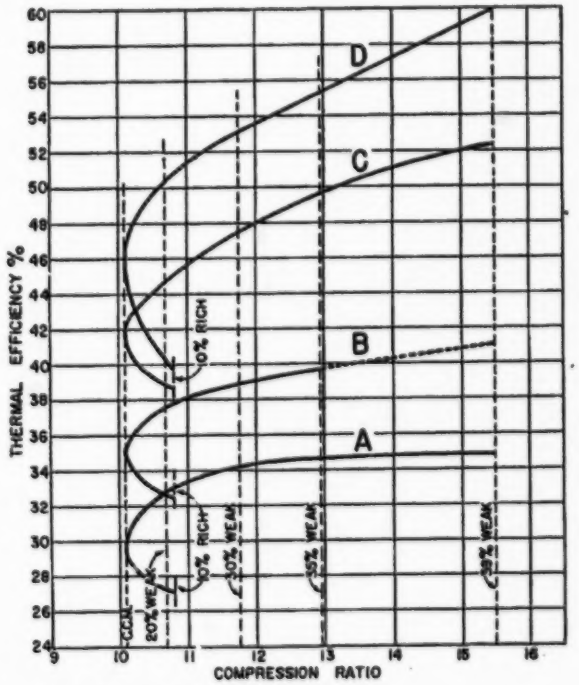

FIG. 6. Observed indicated thermal efficiencies.
Benzene–air mixtures compared with calculated ideal values.
A. Observed, with low heat load.
B. Observed, with higher heat load.
C. Ideal, calculated by "Leah" method.
D. Ideal, calculated by text book method (Pye).

C.R. from 13 to 15½ and a decrease of M.S. from 35 to 39%. The small increase in I.T.E. in the circumstances is attributed to the slow burning of the benzene. Thus for example, the occurrence of maximum combustion pressure 2 to 3° earlier for a mixture 37.7% weak than for one 23.3% weak, Part XXII (5, p. 29, Table II), is attributed to combustion not having been complete at the

piston position at which it was indicated to have occurred. That is, the cycle was changing from constant volume to constant pressure.

The higher values for I.T.E., graph B, are from the data of Fig. 4 for the results of experiments made in the higher heat load conditions and are for the values of C.R. and M.S. for which graph A was obtained. Although two cooler spark plugs, at mid position on the heat scale, were used, the engine would run on weak mixtures for a short period without spark, graph B, Fig. 6. This igniting effect requires further investigation in view of the possibility that the benzene began to decompose to yield diphenyl and hydrogen at the gas temperatures attained at values of the C.R. higher than 13.

Graph C of the figure is for ideal values of thermal efficiency for benzene–air mixtures calculated by the method devised by Leah (7), and modified to allow for engine speed, cylinder dimension, and particular values of the initial temperature of compression. It is assumed however, as in theoretical calculations by others, that the heat of combustion of the benzene is added to the working fluid at constant volume.

Graph D is for ideal values of thermal efficiency as calculated by Pye (10, p. 181) with the use of the most reliable values for specific heats and dissociation available at the time. No allowance was included for engine speed and dimensions. The initial temperature of compression was taken as 212° F. and the calculations were based on a constant volume cycle.

The graphs of Fig. 6 illustrate the increasing rate of departure of real from ideal values of thermal efficiency, with decreasing concentration of benzene in mixtures with air and the consequential decreasing rate of burning of the benzene–air mixture. They show that deductions, based on the assumption that graphs for the variation of ideal and real values of thermal efficiency with compression ratio lie parallel though separated, as made by Pye (10, pp. 181–183) for example, and others, are not justified.

IV. NUCLEAR IGNITION AND THE ADVERSE EFFECT ON THERMAL EFFICIENCY

The adverse effect is exhibited by the graphs of Figs. 7, 8, and 9. These enable a comparison to be made of the values for I.T.E. determined when using pentane, hexane, and heptane in the running conditions required for nuclear ignition, with those determined when using benzene with similar values of C.R. and M.S. and with ignition necessarily by spark. The graphs of the three figures are lettered similarly and the references below will be made accordingly.

The A graphs, for the relation between C.R. and M.S., are of the W form always obtained when the paraffins are used in the conditions required for nuclear ignition. It differs characteristically from the U form obtained for benzene with spark ignition even at relatively high values of C.R., as shown by graph A of Fig. 5.

The B graphs are for values of I.T.E. as determined for the paraffins when used at the values of M.S. and C.R. shown by the A graphs.

The C graphs are for values of I.T.E. determined when benzene was used at the values of C.R. and M.S. shown by the A graphs. The data for the C graphs

were obtained from the family of graphs, Fig. 4, and are extended into the weak mixture region, only until misfiring began.

It is to be remembered that the values given for benzene were determined in the higher heat load conditions in which an approach to a constant volume cycle was obtained for values of M.S. in the neighborhood of correct, and that the value of I.T.E. for any particular M.S. and the corresponding C.R., as taken from the graphs of Fig. 4, was always determined with optimum spark

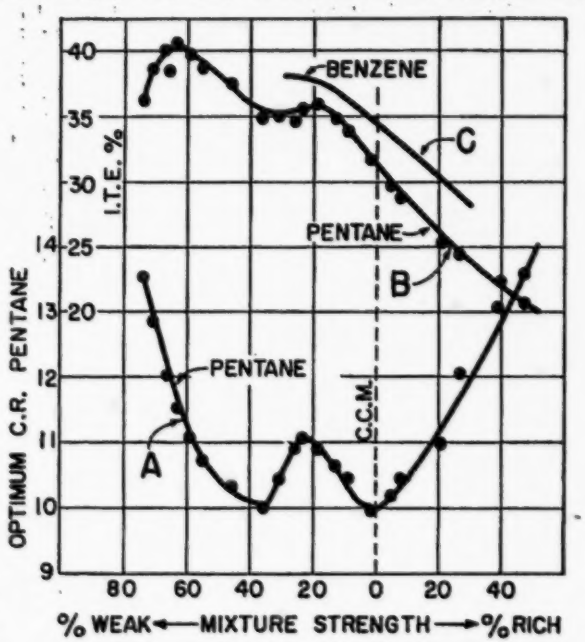

FIG. 7. Comparable values of I.T.E. Pentane with nuclear ignition. Benzene with spark ignition.

timing. The data for the paraffins were obtained when using compression ratios required for nuclear ignition with values always adjusted for maximum power output, that is, to an optimum. The heat of combustion was always added, in the circumstances, to the working fluid at constant volume as illustrated by the indicator diagrams of Fig. 1.

The values for I.T.E. obtained in the circumstances were always lower for the paraffins than for benzene, as shown by the B and C graphs of Figs. 7, 8, and 9. The percentages by which they were lower were 7% for pentane and hexane and 8% for heptane when M.S. was 20% weak. At correct mixtures, I.T.E. for the three paraffins was approximately 10% lower than for benzene.

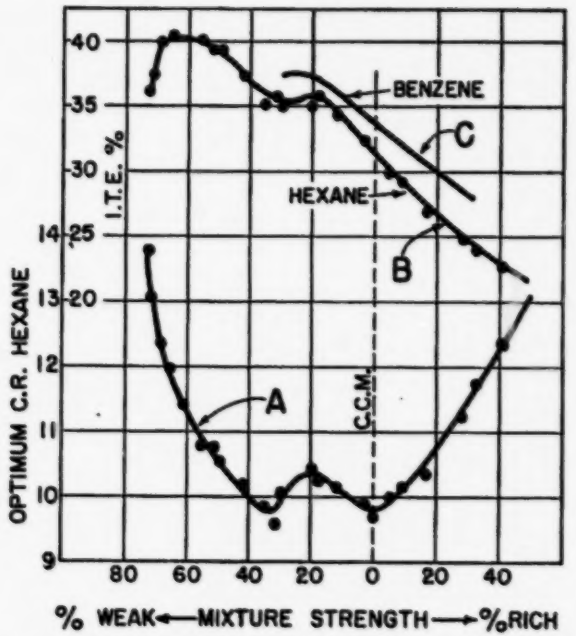

FIG. 8. Comparable values of I.T.E. Hexane with nuclear ignition. Benzene with spark ignition.

The extent to which relative values for I.T.E. were affected by the changes in running conditions that were required to obtain an approach to a constant volume cycle when using benzene may require some consideration.

The most important change was the increase in speed from 400 to 900 r.p.m. The effect on I.T.E. as measured over a higher speed range has been investigated by Ricardo for liquid fuels when used with spark ignition, and found to be negligible, as discussed by Pye (10, p. 205).

When using a paraffin with ignition by *compression* the increase of speed from 400 to 900 r.p.m. would, according to the nuclear theory, have the effect of extending two stage ignition into mixtures richer than 20% weak, with the consequence that I.T.E. for these would be lower than was determined at 400 r.p.m.

The jacket coolant was maintained at 100° F. for the experiments with the paraffins and at 140° F. for those with benzene. It was shown by experiments with town gas, described in Part XII of this series of papers, that the effect on I.T.E. of increasing the jacket coolant by 72° F. was nil. A larger increase of 211° F. led to a *decrease* of 2.5%.

The increase in the temperature of the air supply of from 50° F. to 140° F. for the benzene experiments would raise the temperature of the cycle and consequently be of adverse effect on thermal efficiency.

The increase in I.T.E. obtained on increasing charge density to "normal", when using a paraffin fuel, is discussed in Section VI and shown by the graphs of Fig. 10. An increase occurred when using the weak mixtures in which ignition and combustion occurred in two stages. These mixtures were leaner than any benzene–air mixtures that could be ignited by an electric spark and it was concluded that I.T.E. for benzene was not affected by charge density over the range of mixture strength ignitable by spark.

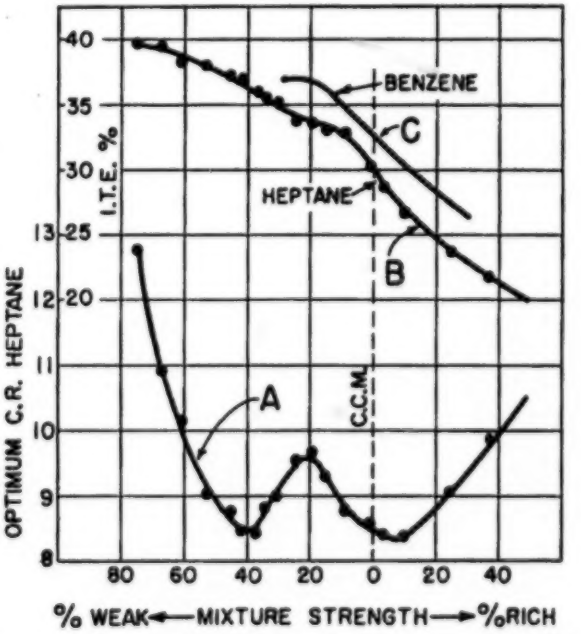

FIG. 9. Comparable values of I.T.E. Heptane with nuclear ignition. Benzene with spark ignition.

V. RESIDUAL PRODUCTS OF THE DECOMPOSITION OF PARAFFIN FUELS

It is shown by the diagrams of Fig. 1 that nuclear ignition of the paraffins used for the experiments occurs in a single stage with mixtures richer than approximately 20% weak. The quantity of very finely divided carbon derived from the cracking of the paraffin would depend on charge density, M.S., C.R., engine speed, and the stability of the fuel molecules. As it would exist in a finely divided state, it would tend to be burned in the flame or to be carried out of the combustion chamber during the exhaust stroke. The amount of deposit remaining in the combustion chamber would then depend mainly on its retention by a film of lubricating oil.

When heptane was used as a fuel, with a charge density of 78% of normal, scattered particles of carbon appeared on the piston crown and patches of carbon on the blind plugs when M.S. was increased to be 20% weak. This was after the engine had run on still weaker mixtures and a brown color had been obtained only on the surfaces mentioned. On further increasing M.S. to the correct value, a very thin and patchy layer of carbon was seen on the piston crown and a nearly uniform layer on the cooler surfaces of the blind plugs. A further increase in the carbon residue was observed when over-rich mixtures were used, Part XXI (6, p. 245).

Observations of carbon residues made recently but with the lower charge density of 64% of normal disclosed that as before, carbon deposits on the piston crown became just visible with mixtures 20% weak, but there was little increase in their density as mixture strength was increased, C.R. always being adjusted to maintain maximum power output.

The engine was used recently for a series of experiments with extremely weak heptane–air mixtures extending over a period of several weeks. Consistent experimental results then ceased to be obtained and the engine was dismantled for inspection. All water cooled surfaces were found to be coated with globules of a resin-like substance varying in size to a maximum of about 1/64 in. in diameter. A similar deposit, but extremely thin, was found on the inlet valve. There was no deposit on the exhaust valve. These deposits could be wiped off easily. The deposits varied in color. They were dark brown on the water cooled surfaces, including the inner ends of the blank spark plugs. There was a similar color on the rim of the piston crown but it tended to turn reddish brown and then to a purplish brown as the center was approached. The deposits not exposed directly to flame tended to build up and become black and gummy. Those on uncovered screw threads of spark plug holes which were not sealed by the unthreaded ends of the blank spark plugs became so hard that a spark plug tap was required for their removal.

A black, very gummy deposit was found on the lands between piston rings and on the faces of the second and third compression rings which had become stuck in their grooves. The oil scraper ring had remained in good operating condition. All grooves of the compression rings were filled with the black gummy deposit. This had hardened to such an extent that the second and third rings could not be removed without being broken. It appeared that the deposits found below the crown of the piston were similar initially to those found in the combustion chamber but that they had become mixed with decomposed lubricating oil and had tended to accumulate and harden when not exposed to oxidizing conditions.

It is well known that aldehyde especially is a product of the combustion of weak mixtures in diesel engines and Webber (13), when discussing methods of maintaining pistons and rings in clean condition, mentions that synthetic resins formed from the aldehyde provide the binding for carbonaceous deposits.

VI. DISCUSSION

Reactions Prior to Ignition

Oxidation or decomposition reactions may occur prior to spark ignition in a carburetor engine, and experiments by others have been carried out in conditions such that oxidation reactions predominate. Thus jackets have been maintained at relatively high temperatures and heat added to the fuel–air mixtures in an attempt to reproduce the temperature conditions of maximum power output at the relatively low compression ratios required to avoid detonation when spark ignition is used. In these circumstances aldehyde is the first oxidation product formed in measurable quantity and its formation is accompanied by a minute proportion of peroxide. The peroxide has been assumed to be responsible in one way or another for the autoignition and the consequent "detonation" obtained on raising the compression ratio when fuels subject to that phenomenon are used. A "motored" engine without spark ignition is used frequently for these experiments.

It appears that Callendar and associates (1, pp. 27–28), 1926, were the first to use a motored engine to demonstrate the formation of aldehydes and peroxides in the temperature condition mentioned. Improved methods of experiment were used by Egerton and associates (2), 1935, in that by means of a sampling valve, the increase in the rates of formation of aldehyde and peroxide during compression were determined while the engine was developing power.

There was little if any publication of results of similar investigations until in recent years the possible effect of preflame reactions on the velocity of combustion in other than piston engines became of interest. Preflame reactions can however be studied most conveniently when using piston engines. Experiments made accordingly, but in temperature conditions suitable for the promotion of oxidation reactions, have been described recently by Retailliau, Ricardo, and Jones (11), by Levedahl and Howard (8), and by Pastell (9). It is mentioned by Pastell that the form of the graph, Fig. 4, of his paper may be due to endothermic cracking reactions.

Method Used During Compression to Promote Decomposition Reactions Only

The method was devised to avoid surface oxidation of the fuel during compression and to make possible the use of paraffin fuels at compression ratios such that the temperatures and pressures attained by the end of compression would approach those of the end gas with ignition by spark. Autoignition would then, at a suitable high compression ratio, be initiated in some part of the whole charge instead of in some part of the end gas only.

Oxidation was avoided by the use of operating conditions required for an exceptionally low heat load as described in Section I. The surface in the combustion chamber which, in the absence of a spark plug, would attain the maximum temperature was that of the exhaust valve. Its mean temperature was shown by separate experiments to be approximately 625° F. (329° C.) when the engine was running on autoignition, a correct heptane–air mixture, and the C.R. required for maximum power output. The temperature fell rapidly to 330° F. (165° C.) approximately as M.S. was reduced to 20% weak. The low heat load of the experiments was due in part to a reduction of charge density, generally to 64% of normal. This, in addition, had the effect of reducing the pressure due to autoignition to an extent that could be tolerated by the engine. Thus it was possible to measure the indicated thermal efficiency corresponding to the maximum power output for any ignitible mixture and to compare the values with those obtained when using a fuel such as benzene which did not decompose in the engine to provide material nuclei of ignition.

The Adverse Effect of Decomposition on Thermal Efficiency

The heat of compression would be insufficient, on the basis of published values for the "energy of activation", to decompose the whole of the fuel in a mixture even 20% weak to the extent required to produce finely divided carbon as nuclei of ignition. The values were obtained for vapors unmixed with air, contained in glass reactors, externally heated. They may not apply to engine conditions in which the vapor is mixed with air and heated rapidly by compression. It may however safely be assumed, in the absence of relevant data, that, as stated in Part XX (4, p. 39), decomposition of the fuel to the extent necessary to produce nuclei of ignition would occur in the part of the charge which had attained a higher than average temperature. That would be the part adjacent to the hot exhaust valve. It is not yet clear whether the rapid combustion which follows the nuclear ignition of this part of the charge is due to the consequent pressure wave or to a thermal process initiated by a relatively large volume of flame. The process of the nuclear ignition and subsequent combustion of the charge occurred in approximately 3° of crank revolution when a correct heptane–air mixture was used at a C.R. of 8.5, Fig. 1. That would be in 0.00125 sec., and a comparison of the values of I.T.E. obtained accordingly with those for the relatively slow burning benzene presents some difficulty. Thus we obtained a value of 31% for I.T.E., when using a correct benzene–air mixture at a C.R. of 7.0, and a heat load such that preignition did not occur (5, p. 33). Ricardo, using a heat load estimated to have been 40% greater, obtained 37% for the I.T.E. at a C.R. of 6.9, but could not use a higher value because of the onset of preignition (12, pp. 144–145). Furthermore it will be seen by reference to Fig. 6 that an increase of heat load from a relatively low value to the maximum used for the experiments with benzene described in this Part led to an increase in I.T.E. of from 29.5 to 35%, at a C.R. of 10. This increase was shown by experiment to be due to the heat of combustion of the benzene having been added to the working fluid at more nearly constant volume. It is to be noted here that the increase occurred in spite of the decrease that would be expected because of the higher temperature

of the cycle. The heat of combustion of the paraffin is shown by the indicator diagrams of Fig. 1 to have been added to the working fluid at constant volume for mixtures within the range correct to 20% weak. It may be concluded therefore that higher values for I.T.E. than those observed would have been obtained for benzene–air mixtures if it had been possible to use a higher heat load without the onset of preignition. The result would be that a greater adverse effect on thermal efficiency than that observed could then be attributed to the heat absorbed by the decomposition reaction required for the nuclear ignition of the paraffin–air mixtures. This, as shown by the B and C graphs of Figs. 7, 8, and 9, accounted for the values of I.T.E. for the paraffins being from 7 to 10% lower than those for benzene, in similar conditions of M.S. and C.R.

The Nuclear Theory of Ignition

The theory was developed, as described in Part IV (3), to account for the autoignition of the end gas in spark ignition carburetor engines. It was therefore applied only to fuel–air mixtures richer than 20% weak because spark ignition tends to be ineffective as mixture strength is further reduced. Autoignition with mixtures richer than 20% weak was attributed, according to the theory, to the igniting effect of finely divided carbon derived from the cracking of the fuel at the temperature and pressures attained by the end gas, and residues of the carbon always appeared on the piston crown.

It is significant that, when using mixtures leaner than 20% weak, formaldehyde was detectable in the exhaust and residues of a resinous nature appeared on the piston crown, Part XXI (6, pp. 246–247), and that, after a long period of running on weak mixtures, residues which appeared to be a mixture of resins and carbon had the effect of sticking piston rings firmly in their grooves, Section V.

The surfaces in the combustion chamber of the C.F.R.-F2 engine do not attain temperatures required for the oxidation of the paraffins to aldehyde in the low heat load conditions of the experiments even when correct mixtures are used. This statement is based on temperature measurements which will be described in a subsequent Part. However, on decreasing M.S. and raising C.R. to maintain optimum power output, there is a further decrease in heat load, which depends mainly on the heat of combustion; thus surface temperatures decrease while the temperature of the charge increases. The aldehyde always present in the products of the combustion of weak mixtures must then have been formed on the carbon nuclei present in the charge as a result of the cracking of the paraffin. The compressed mixture may then contain nuclei of finely divided carbon and nuclei composed of a mixture of resins and carbon, which differ in degree of inflammability. This difference affords an explanation for the occurrence of two-stage ignition in mixtures leaner than 20% weak, in the conditions of the experiments described in this Part.

This extension of the nuclear theory of ignition, although regarded at present as a working hypothesis, appears to afford an explanation for the characteristics of the two-stage ignition of mixtures leaner than 20% weak.

Nuclear Ignition and the Lower Limit of Inflammability

The indicator diagrams of Fig. 1 show that the nuclear ignition of heptane, taken as a typical paraffin, occurred in a single stage when mixtures with air richer than 20% weak were used. It is indicated by experiments described earlier that the nuclei of ignition were those of finely divided carbon. Ignition began to occur in two stages when weaker mixtures were used. It will be seen by reference to the graphs of Figs. 7 to 9 that this double igniting effect continued to be effective until the paraffin–air mixtures were from 70 to 80% weak. This was not the limit. In other experiments, Part XXI (6, p. 244) with heptane as the fuel, nuclear ignition continued, as C.R. was always raised to an optimum value as M.S. was diminished until it became 93% weak. The air–fuel ratio was then 220 : 1 by weight and the Opt. C.R. 22.8. The power developed was not sufficient to run the engine at the speed of the experiments, 400 r.p.m., and the deficiency in power was supplied from the dynamometer used as a motor. Heptane was used for these experiments because it decomposes more readily than hexane or pentane to supply nuclei of ignition.

The experimental results show that the enormous extension of the lower limit of inflammability of the paraffin–air mixtures was not due fundamentally to the high temperatures and pressures attained on increasing C.R. Thus it occurred solely when using the fuels which could be decomposed to provide material nuclei.

Characteristics of Two Stage Nuclear Ignition; Mixtures Leaner Than 20% Weak

The mixture range 20 to 40% weak was marked by the advent of two-stage ignition, the occurrence of formaldehyde in the exhaust, the appearance of residues of combustion which appeared to be mixtures of resins and carbon, a decrease in the C.R. required to maintain optimum power output, and a tendency for I.T.E. to remain constant. A nearly constant value was obtained when using hexane and pentane and an approach to such a value when using heptane, see Fig. 3. The nearly constant value for I.T.E. can be accounted for, as mentioned earlier, by the increase due to decreasing M.S. being offset by the decrease due to decreasing values of Opt. C.R. The decrease in Opt. C.R. is attributed, according to the extension of the nuclear theory, to the compressed charge containing two types of nuclei, namely, those of finely divided carbon and others consisting of mixtures of carbon and resins. The latter being the more inflammable would initiate a first stage of ignition which would cause and be followed immediately by a second stage depending on the less inflammable nuclei of finely divided carbon.

The increase of C.R. required to maintain optimum power output when using mixtures leaner than 40% weak is regarded as being required to maintain a necessary first stage of ignition. The first stage, on this basis, must be considered as a "primer" for the second stage.

The values of I.T.E. for mixtures leaner than 40% weak rose slowly in relation to the increase of C.R. required to maintain optimum power output. A maximum value of 40% for I.T.E. was obtained when mixtures were 65%

weak. There was then a rapid decrease in I.T.E. as mixtures leaner than 65% weak were used, although C.R. was raised rapidly in order to maintain an optimum value. Thus I.T.E. had fallen to 34% and Opt. C.R. had risen to 15.5 when the mixture became 80% weak.

The relatively low values for maximum I.T.E. obtained in the low heat load conditions of the experiments can be explained as follows: The heat due to combustion of the fuel decreases proportionally to the decrease in M.S., with the consequence that the mean temperatures of the surfaces in the combustion chamber decrease and an increasing proportion of the heat of compression is absorbed by them. An abnormal increase in Opt. C.R. is then required to raise the temperature of the gaseous charge to that required for decomposition of the paraffin to the extent required for the provision of nuclei of ignition. The *quantity* of heat available during compression can however be increased by increasing charge density, without increasing the temperature, if compression ratio remains unchanged. Thus an increased proportion of the

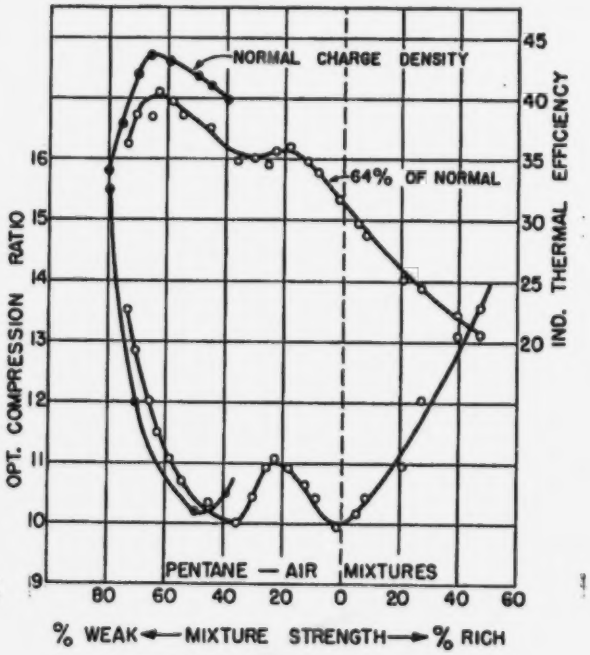

FIG. 10. Effect of increase of charge density to increase I.T.E.
● Normal charge density.
○ 64% of normal.

heat of compression would be available for the decomposition reaction and for conversion into power with a corresponding increase in I.T.E.

An experiment was tried accordingly with a charge density of "normal", obtained by using the standard C.F.R. carburetor fitted with a 9/16 in. diameter venturi instead of the choke tube used to obtain 64% of normal charge density. It is estimated that an increase of charge density of 33% was obtained. The other running conditions were not changed, that is, engine speed was maintained at 400 r.p.m., the jacket coolant at 100° F., and the air supply at 50° F. Beginning with a mixture 80% weak, it could be increased to 40% weak before the occurrence of an intolerable intensity of knocking combustion. The results of the experiments are exhibited by the graphs of Fig. 10. They show that maximum I.T.E. increased by approximately 9% on increasing the charge density while the corresponding Opt. C.R. decreased from 11.7 to 11.1, and it appears that with the greater available quantity of heat, the increase of I.T.E. was obtained with a lower compression temperature.

CONCLUSION

The method used for the experiments with the paraffins has made possible the investigation of the gas phase reactions required for ignition by compression and the nature of these as affected by mixture strength. The experimental work is regarded as being of a preliminary nature. Further data relating to two-stage ignition, surface temperatures, and the mechanism of decomposition of fuels in engine conditions are required for a more complete understanding of the fundamentals of combustion as it occurs in engines.

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